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CONTINUOUS AUTOMATIC BEAMHOUSE PROCESSING III. EFFECTS OF PROCESSING CONDITIONS ON THE RAPID SOAKING AND UNHAIRING OF CATTLEHIDES*

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Abstract

Rapid soaking and unhairing of brine-cured cattlehides are integral functions of the continuous automated beamhouse process developed at the Eastern Regional Research Center of the U.S. Department of Agriculture. Experiments in the continuous beamhouse pilot plant facility determined that effective unhairing in 10 mins could be accomplished with 4%-6% Na_2S (100% basis). Lower Na_2S concentrations required longer contact times or control of salt levels in the unhairing liquor. Estimates of chemical and water use are also presented.

Introduction

Developments in the tanning industry over the last several decades have increased the need for research in tannery processes to address the questions of solid and liquid waste management, water usage, and production efficiency. The Engineering Science Laboratory of the Eastern Regional Research Center (ERRC) has developed the continuous beamhouse process whose features have been described previously (1, 2). The continuous beamhouse process represents a significant departure from conventional treatment in that short soak and unhairing times are used, automatic hide conveyor systems are utilized, and continuous steady state processing is introduced.

This paper will examine the nature of the soaking and unhairing operations of the process. As reported by Komanowsky *et al.* (2), basic research has demonstrated that effective hair pulping with sodium sulfide could be achieved in contact times on the order of 10 min. By taking advantage of high rates of diffusion in the early stages of soaking, the salt content of the hide could be lowered to levels which would not impede the unhairing action. This paper will present the results of a pilot plant study of the soaking and unhairing variables and their effects on the rapid unhairing of brine-cured cattlehides. The influence of these variables on hide swelling and rehydration will also be presented. The ERRC

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continuous beamhouse pilot plant line utilizes sided cattlehides which were eventually processed into crust leather by traditional methods. Future papers will discuss the physical, chemical, and qualitative characteristics of the blue stock and crust leather produced in this study.

EXPERIMENTAL

The ERRC pilot plant facility has been previously described (1). The line has a nominal capacity of 18 sides/hr for the soaking and unhairing operations. The pilot plant facility has the capability for automatic mechanical unhairing and fleshing following the soaking and unhairing steps. For experiments reported herein, hides were manually placed on the loading conveyor, processed through two soaking and one unhairing vats, and then either removed from the hide transport conveyor and manually loaded onto a second conveyor for mechanical unhairing and fleshing or placed into a hide processor (Challenge-Cook Brothers, Model HP12)[§] or drum for further processing. If a drum or hide procesor was used, the pulped hair was first removed in a 5 min lime water wash. Processing conditions for the subsequent operations of reunhairing (optional), reliming, bating, pickling, and tanning are given in Table I. When the unhairing and fleshing machines were operated, a lime water solution was recirculated as a spray onto the rolls of both machines to minimize H_2S release from the pulped hair.

With respect to conditions inside the hide, the continuous beamhouse soaking and unhairing operations are nonequilibrium processes. This paper will report the results of experiments designed to investigate the effects of the process variables (including time). The objective of this study is to determine the range of conditions suitable for rapid soaking and unhairing. In all, this pilot plant study consisted of 44 experiments involving 389 sides and was conducted over the course of 1½ years. The hides were processed to the blue in ERRC facilities; subsequently, the blue stock was converted to crust leather by a contract tanner according to his standard process.

Experimental Design

Previous bench scale experimental work (2) had established that rapid unhairing could be accomplished with Na_2S solutions at hide salt concentrations of 8-9 percent (wet basis) or lower. Using this range as a criterion for salt removal prior to unhairing, a mathematical model of unsteady state salt diffusion (3) predicted that, for 10 min soaking times in each of two baths, the salt concentrations for steady state operation should be 10 percent NaCl (w/v) and 4 percent NaCl

[§]Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

TABLE I

CONDITIONS FOR POST CONTINUOUS BEAMHOUSE PROCESSING OPERATIONS

Step	Float composition[a]	Time, hr	Processing conditions
Reunhair (optional)	100% H_2O, 2.3% Lime 1.7% Na_2S	2	85°F, 30 Min mixing/hr @4 rpm
Relime	100% H_2O, 2.5% Lime	16-20	85°F, 10 Min mixing/hr @4 rpm
Relime wash #1	100% H_2O	1	85°F, Continuous mixing @4 rpm
Relime wash #2	100% H_2O	1	90°F, Continuous mixing @4 rpm
Bate	100% H_2O, 3.3% $(NH_4)_2SO_4$, 0.09% Oropon WN-4, 0.15% Triton X-114	1.75	90°F, Continuous mixing @10 rpm
Post-bate wash #1	100% H_2O	0.5	85°F, Continuous mixing @10 rpm
Post-bate wash #2	100% H_2O	0.5	85°F, Continuous mixing @10 rpm
Pickle	50% H_2O, 1.5% Sodium formate, 8% NaCl, 1.5% H_2SO_4	1.5 16-18	85°F, Continuous mixing @10 rpm 85°F, 3 Min mixing/hr @10 rpm
Tanning	10% H_2O, 8% Tanolin R added to pickle float	3.5 hr	90°F, Continuous mixing @12 rpm
Neutralization	Progressive addition of sodium biocarbonate up to ½-1%, pH 3.8-4	0.5-1	90°F, Continuous mixing @12 rpm
Wash	80% H_2O, 0.1% Kathon LP	5 min	80°F, Continuous mixing @8 rpm

[a] Chemical dosages based on raw hide weight through relime washes, thereafter based on limed hide weight. Chemical dosages are reported as percentage of the technical grade chemical.

(w/v), respectively. These concentrations were maintained throughout the course of the study.

The specific variables which were investigated in controlled pilot plant studies are listed in Table II. The range of each variable was determined from bench scale research or early screening experiments in the pilot plant line. Three min. is the minimum hide residence time in each vat while 10 min. represents the original design criterion for the rapid unhairing operation. The salt content of the unhairing tank would vary during steady state operation due to salt diffusion from the hides, thus making it necessary to investigate the effect of salt level in Na_2S unhairing liquors.

TABLE II

PROCESS VARIABLES FOR RAPID UNHAIRING

· Sulfide concentration	1.5-6.5 Na_2S (w/v)
· pH	12.8-13.8
· Salt content of unhairing bath	5-11% (w/v)
· Time	3-20 min.

The experimental plan incorporated principles of factorial design. For unhairing with Na_2S (pH = 13.8), the following unhairing bath compositions were employed:

6.5 percent (w/v) Na_2S,* 5 percent (w/v) NaCl
2.0 percent Na_2S, 5 percent NaCl
2.0 percent Na_2S, 11 percent NaCl
6.5 percent Na_2S, 11 percent NaCl

At each unhairing bath composition a minimum of six sides were processed at two soaking and unhairing times, 3 min and 10 min.

The effect of pH of the unhairing bath was studied through additional runs at pH 12.8, 13.2, and 13.5. In these runs, soaking and unhairing times were 20 min. (total) and 10 min., respectively, and the total sulfide content was equivalent to 6 percent Na_2S. These runs were conducted at no added salt in order to observe the effect of pH. The initial run of this series was at pH 12.8 and the bath contents were prepared from a sulfide solution that was the product of an H_2S flash vaporization-reabsorption system, using a NaOH solution as the reabsorbing liquid. Higher pH values for subsequent runs were achieved by addition of appropriate amounts of 50 percent NaOH to the bath.

*Throughout this paper Na_2S concentrations are reported as the concentration of the pure chemical.

Experimental Procedures

Before each pilot plant run, prefleshed brine-cured cattlehides obtained from local sources were sided, weighed, and stamped for identification. The sampling area on the hide was shaved and an initial sample was taken. The sampling area was near the neck of the hide along either the backbone or belly. Hides were processed with no further pretreatment.

Operational details of the continuous beamhouse pilot plant line are reported elsewhere (1). In the preparation of the soaking tanks a bactericide, Sterozol S (Hamblet & Hayes, Salem, MA) was added at a concentration of 0.15 percent. No other soaking aids were utilized. The pilot plant is equipped with an H_2S monitoring system (Texas Analytical Controls, Houston, TX). Ambient H_2S levels during normal operation never exceeded 1.0 ppm.

Sampling and Analytical Methods

Since the soaking and unhairing operations in the pilot plant runs took place under steady state conditions with respect to the soaking and unhairing baths, effects of process conditions could only be observed by following changes in hide properties. Accordingly, hide samples were taken after each treatment step. This sampling consisted of a hide thickness measurement and a hide sample for determination of moisture and chloride contents. The degree of hair pulping was also noted.

Throughout the course of the study, a group of three sides represented the basic unit of hides for processing, analysis, and evaluation. This was done so that differences due to the variability among hides could be separated from the effects of treatment variables. From each group of three sides, one was selected for sampling and subsequent analysis as described above.

Salt concentrations of aqueous samples were obtained from chloride measurements determined by the Mohr method (4). In solutions containing sulfide, the sulfide was oxidized with hydrogen peroxide prior to chloride analysis. Sulfide analyses were performed according to the method of Booth (5).

Moisture and chloride contents of hide samples were performed as follows. Diced hide samples were vacuum dried at 70°C for 16 to 18 hr and the weight loss calculated as moisture content. The diced samples were then ground in a Wiley mill to pass a 10-mesh screen, weighed into porcelain dishes, and ashed at 550°C. The ash was hydrolyzed and chloride was determined by the Mohr method. All analytical determinations were performed in duplicate.

pH measurements of sodium sulfide solutions containing salt are subject to error due to the high level of sodium ion. This was overcome by standardizing the pH meter with pH standards to which was added an amount of salt equal to that in the sample.

Results and Discussion

One configuration of continuous beamhouse processing technology could involve splitting of hides in an unswollen state after rapid unhairing, mechanical unhairing, and fleshing. It was felt that the split would be more uniform and significant savings in downstream tanning operations could be realized. Results of hide thickness measurements (Table III) reveal minimal swelling, less than 10 percent, over a wide range of hide thicknesses. Swelling is low because of the incomplete salt removal during soaking.

TABLE III

HIDE SWELLING IN CONTINUOUS BEAMHOUSE TREATMENT[a]

Initial hide thickness, oz (range)	Swelling[b] (%)
7.0-7.9	9.5
8.0-8.9	8.4
9.0-9.9	5.6
10.0-10.9	3.8

[a] Measurements taken after unhairing.
[b] From actual thickness measurements in neck area along backbone or belly.

The goal of the continuous beamhouse soaking operation is to produce conditions at the hide surface suitable for unhairing in 10 min. Thus, soaking conditions in the continuous beamhouse process differ greatly from conventional soaking operations in the soaking time, float rates, degree of mixing, and mechanical equipment utilized. Hide salt removal data as a function of soaking and unhairing times in the pilot plant experiments are reported in Table IV. Statistically, the only significant differences among the mean hide salt contents are the values at 16 and 30 min. total soaking time as compared to the 9 min. value (students t test, 95% confidence level). Based on these results, it can be

TABLE IV

SALT REMOVAL FROM HIDES DURING RAPID SOAKING AND UNHAIRING

			Hide salt content (wet) after unhairing[a]		
Soak time min	Unhair time min	Total soak + unhair time, min	Mean value	Std. dev.	No. of hides
3	3	9	9.40	1.06	9
3	10	16	7.92	1.21	6
10	3	23	8.67	1.12	12
10	10	30	8.30	1.13	31

[a] Initial hide salt content = 12% - 15%.

calculated that 25-35 percent of the initial hide salt is removed in the soaking and unhairing operations, reducing the average hide salt concentration to approximately 8-9 percent (wet basis). This range represents the target hide salt content for effective rapid unhairing with Na_2S as reported by Komanowsky *et al.* (2).

Salt removal from a brine-cured hide is intimately related to the process of hide rehydration which is important for proper liming action and subsequent tanning. Figure 1 illustrates the differences in salt removal and rehydration phenomena for hides processed conventionally versus those treated via continuous beamhouse processing. The continuous beamhouse hides underwent a 2 hr reunhairing and a 16 hr reliming following the continuous beamhouse operations. These results were part of an extensive matched side study investigating the effects of rapid soaking and unhairing on finished leather quality. The high rate of salt removal for continuous beamhouse treated hides is primarily due to the high effective float ratios of approximately 50 lb float/lb hide during soaking. While hide rehydration occurs much more rapidly, full "opening up" and liming action is allowed to occur as in a conventional process. As Figure 1 demonstrates, the hide processing which utilized continuous soaking and unhairing achieved the same degree of salt removal and rehydration in approximately half the time.

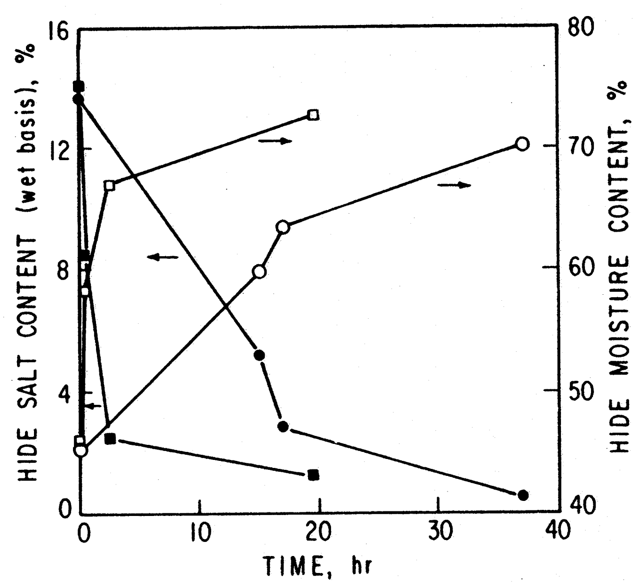

FIGURE 1. — Rehydration Phenomena in conventional and continuous beamhouse processing—A matched side study. □, ■ refer to hides treated via continuous beamhouse processing (see text for details). 0, ● refer to hides processed as follows: soak, 100% float, 15 hours; unhair, 100% float, 2 hours; relime, 200% float, 20 hours. Data represent averages of values from two hides.

The rapid unhairing step in continuous beamhouse processing must meet the requirement that the hair be sufficiently pulped that it could be easily removed by a mechanical unhairing operation. One purpose of the pilot plant studies was to determine the range of unhairing conditions under which this contraint could be met while producing leather of commercially acceptable quality. Previous research in this laboratory and elsewhere (6) had indicated that Na_2S solutions in the range of 2-6.5 percent (w/v) could meet the objectives stated above. The unhairing variables to be considered in a continuous process are sodium sulfide concentration, pH, and the level of salt in the unhairing liquor. Due to the lack of equilibrium conditions relative to salt in the hide and unhairing bath, the possible retarding effects of high salt concentrations must be considered.

A summary of the pilot plant experiments utilizing Na_2S as the unhairing agent (pH = 13.8) is presented in Table V. These experiments indicate that as the salt concentration in the unhairing liquor increases, the minimum Na_2S concentration for effective hair pulping in 10 min. increases. At Na_2S concentrations of approximately 4-5 percent (w/w) or higher, salt concentrations of up to 10 percent (w/w) have no observable effect. At Na_2S levels of 1.5-2 percent salt contents exceeding 4 percent begin to affect the unhairing rate and require progressively longer times for sufficient hair pulping. However, observations of the hide immediately after unhairing indicated that the epidermis was not attacked under the unhairing conditions employed and thus damage to the underlying grain layer would not be expected. It should be pointed out the effects of unhairing bath composition on final leather quality are not considered here and will be covered in a later publication. Also, the choice of the composition of the unhairing liquor in a continuous operation may be partially dictated by operational considerations and size of the processing line. These factors will be discussed later in this paper.

The pH of the unhairing liquor has the most dramatic effect on the degree of hair pulping in a rapid unhairing operation. The pH of the unhairing bath can be

TABLE V

SUMMARY OF PILOT PLANT EXPERIMENT UTILIZING Na_2S at PH 13.8

Unhairing bath composition		Unhairing time, min.	Observations	Number of sides processed
$[Na_2S]^a$, %	$[NaCl]^a$, %			
5.1-6.1	3.7-4.3	3-10	Hair well pulped	82
5.6-6.0	8.9-9.5	3-10	Hair well pulped	26
1.6-2.1	4.1-4.6	3	Small areas of stubble in blue stock	21
		10	Hair well pulped	45
1.4-1.7	8.7-9.9	3	Insufficient hair pulping	12
		10	Marginal hair pulping; some stubble	33
		22	Hair well pulped	3

[a] Concentrations are expressed as w/w.

changed by utilizing mixtures of sodium sulfhydrate (NaHS) and sodium sulfide. It was desired to determine the range of acceptable pH values for unhairing in the continuous beamhouse process. Pilot plant experiments were performed with unhairing baths of various pH's which were prepared as described in the experimental section. Results of these experiments (Table VI) demonstrate that a minimum pH of 13.5 is necessary for a rapid unhairing operation in order to insure effective hair pulping. The pH effect described here is consistent with the "ß-elimination" interpretation of the mechanism of unhairing (7, 8) in that as the pH decreases the concentrations of hydroxyl ion and especially sulfide ion decrease, slowing the rate limiting step.

TABLE VI

EFFECT OF PH ON RAPID UNHAIRING[a]

Run #	Total S (% as Na_2S)	pH[b]	Observations
29	5.8	12.8	Hair not pulped
30	5.7	13.2	Hair marginally pulped, some stubble in blue stock
31	5.5	13.5	Hair well pulped

[a] 10 min. unhairing time, salt content of unhairing bath = 0.
[b] Equivalent to unhairing baths of the following compositions
pH 12.8: 13% Na_2S, 87% NaHS
pH 13.2: 33% Na_2S, 67% NaHS
pH 13.5: 50% Na_2S, 50% NaHS
percentages are molar percentages and are derived from equilibrium calculations.

Future publications will report the effects of continuous beamhouse processing on the final leather quality and the results of extensive matched side studies that compared processes incorporating continuous automatic soaking and unhairing to standard tannery treatments.

Operational Considerations

The pilot plant experiments reported herein have provided valuable information in two areas: the change of key hide properties during rapid soaking and the effects of unhairing variables on hair pulping. For obvious reasons it was not possible to operate the pilot plant line at the hide processing rates of commercial tanneries. However, reasonable extrapolations from our data can be made to estimate chemical usages and to discuss operational aspects of a commercial continuous beamhouse processing line.

Water usage in a two-stage soaking operated with countercurrent fresh water flow is estimated to be 0.4 lb H_2O/lb hide. Water usage in a countercurrent system is proportional to the degree of salt removal. The above figure of 0.4 lb H_2O/lb hide is based upon 25 percent removal of salt from a 50-lb hide initially at

14 percent salt and would result in a hide salt content after soaking of 8.5 percent (wet). When all beamhouse operations through relime are considered, hides soaked and unhaired in the continuous beamhouse process followed by drum reliming would require 30-60 percent less water than a typical drum process (the "USDA" process), depending on the relime conditions employed. The water savings is due to the countercurrent use of water in the continuous soaking operation.

Based on the limited data available, sulfide usage in a rapid unhairing operation should be approximately equal to that of a conventional process. This is not unexpected if the unhairing step, whether hair burning or pulping, is viewed as a sulfide consumption reaction. Decisions regarding the makeup of Na_2S to the unhairing tank, or its total replacement, are dependent upon several factors, such as whether or not a sulfide recovery system is to be utilized, the size and capacity of the production line, and the degree of salt removal prior to unhairing (which affects the rate of salt buildup in the unhairing liquor).

Summary

This paper has described a pilot plant research study of the rapid soaking and unhairing operations of the ERRC continuous beamhouse processing facility. Results have demonstrated that effective unhairing of brine-cured cattlehides can be accomplished in 10 min. with 4-6 percent (w/w) Na_2S. Concentrations as low as 1.5 percent Na_2S may be utilized if slightly longer times are employed or if the salt level in the unhairing liquor is controlled.

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